

## Analysis of thermal expansivity of alkali halide crystals

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**Abstract** : The temperature dependence of thermal expansivity and interionic separations have been studied in the present paper for eight alkali halide crystals viz. NaF, NaCl, KCl, KBr, KI, RbCl, RbBr and RbI. The expression for interionic separation obtained earlier by Kumar [*Physica B* 205 175 (1995)] has been corrected so as to make it compatible with the value of thermal expansivity at initial temperature. The values of interionic separation as a function of temperature calculated in the present study using the modified formulation are found to present close agreement with the experimental data for the alkali halides upto their melting temperatures.

**Keywords** : Thermal expansivity, alkali halides, interionic separation

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### 1. Introduction

Thermal expansivity  $\alpha$  is a very important physical quantity for understanding the thermoelastic behaviour and equation of state for solids at high temperatures [1-4]. Attempts have been made to develop theoretical models based on first-principle methods for calculating  $\alpha$  at high temperatures [5-8]. The results obtained from these methods at high temperatures deviate substantially from the experimental values. The empirical methods [9,10] are still useful for predicting thermal expansivity of solids at high temperatures upto their melting temperatures. The thermal expansivity data of solids at high temperatures are the basic requirements for computing thermoelastic properties of solids at different temperatures [11].

The thermal expansivity  $\alpha$  for many solids has been found [1,12] to increase linearly in an approximate manner with the increase in temperature at  $T > \theta_D$ , the Debye temperature. For alkali halides to be considered in the present study viz. NaF, NaCl, KCl, KBr, KI, RbCl, RbBr and RbI, we have the values of  $\theta_D$  which are close to or less than the room temperature value  $T_0 = 300$  K [13]. Therefore, the variation of  $\alpha$  for these crystals is expected to be approximately linear for the entire range of temperatures from room temperature upto their melting temperatures  $T_m$ . The melting temperatures of the alkali halides

are about 1000 K, which are 3 to 6 times of their Debye temperatures. We have thus a very wide range of temperatures from  $T = \theta_D$  to  $T = T_m$  for studying the thermal expansivity of alkali halides. Kumar [14] has developed a formulation for studying the temperature dependence of  $\alpha$  of alkali halides using the linear relationship between thermal expansivity and temperature. It is shown here that this relationship does not satisfy the initial boundary condition. The formulation given by Kumar has been revised in the present study. The effect of this modification is then studied by calculating  $\alpha$  and interionic separation as a function of temperature. Formulation and analysis are presented in Section 2. Results are discussed and compared with the experimental data in Section 3.

### 2. Formulation and analysis

The experimental values of  $\alpha$  for NaCl and KCl at different temperatures have been listed by Anderson [1] and Yamamoto *et al* [15] from the original work due to Enck *et al* [16] and Enck and Dommel [17]. These experimental data are plotted in Figure 1. The variations of  $\alpha$  with  $T$  are found to be almost linear for NaCl as well as for KCl. The similar behaviour is expected also for other alkali halides. Kumar [14] has developed a formulation using the linear relationship

$$\alpha = \alpha_0 + \alpha' T, \quad (1)$$

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where  $\alpha_0$  is the value of  $\alpha$  at  $T = T_0$ , the room temperature taken as the initial temperature, and  $\alpha' = d\alpha/dT$ . Using eq.(1),

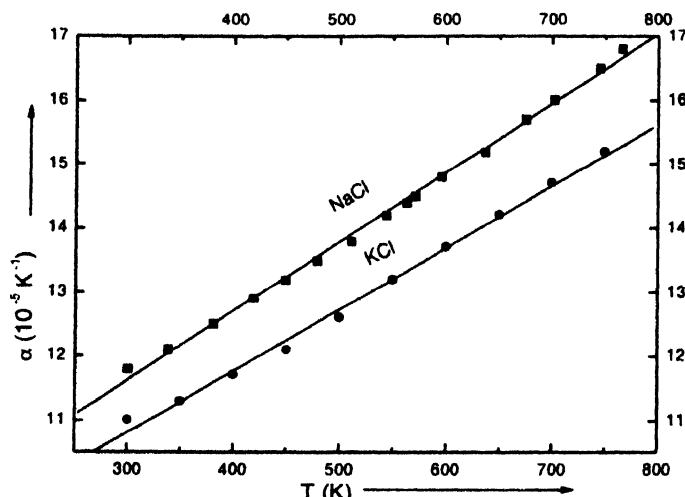


Figure 1. Plots of thermal expansivity  $\alpha$  ( $10^{-5} \text{K}^{-1}$ ) versus temperature  $T$  (K) for NaCl and KCl using the experimental data [16, 17].

Kumar obtained an expression for the interionic separation  $r$  as a function of temperature, which is given below :

$$r = r_0 \exp \left[ \frac{1}{3} \left\{ \alpha_0 (T - T_0) + \frac{1}{2} \alpha' (T^2 - T_0^2) \right\} \right], \quad (2)$$

where  $r_0$  is the value of  $r$  at  $T = T_0$ . Values of  $\alpha'$  were determined by Kumar using the Anderson-Gruneisen parameter  $\delta_T$  and the pressure derivative of isothermal bulk modulus  $K_T$ .

It should be pointed out here that eq.(1) is not consistent with the initial boundary condition viz.  $\alpha = \alpha_0$  at  $T = T_0$ . In order to satisfy this condition, we have to modify eq.(1) as follows :

$$\alpha = \alpha_0 + \alpha' (T - T_0). \quad (3)$$

We have revised the formulation given by Kumar [14] using eq.(3) in place of eq.(1).

The coefficient of volume thermal expansion or simply the thermal expansivity  $\alpha$  is defined as

$$\alpha = \frac{1}{V} \left( \frac{dV}{dT} \right)_P. \quad (4)$$

Thus at constant pressure, the following differential equation is obtained, using eqs.(3) and (4):

$$[\alpha_0 + \alpha' (T - T_0)] dT = \frac{dV}{V}. \quad (5)$$

On integrating eq.(5) along an isobar, we get

$$\alpha_0 (T - T_0) + \frac{1}{2} \alpha' (T - T_0)^2 = \ln (V/V_0), \quad (6)$$

where  $V_0$  is the value of volume at  $T = T_0$ , the room temperature. In deriving eq.(6), it has been assumed that  $\alpha' = d\alpha/dT$  remains constant. The fact that this assumption holds good for NaCl and KCl is evident from Figure 1. Eq.(6) can be rewritten as follows

$$V = V_0 \exp \left[ \alpha_0 (T - T_0) + \frac{1}{2} \alpha' (T - T_0)^2 \right]. \quad (7)$$

The volume  $V$  is related to the lattice parameter or interionic separation  $r$  such that

$$V/V_0 = (r/r_0)^3, \quad (8)$$

where  $r_0$  is the value of interionic separation  $r$  at  $T = T_0$ . Eqs. (7) and (8) then yield

$$r = r_0 \exp \left[ \frac{1}{3} \left\{ \alpha_0 (T - T_0) + \frac{1}{2} \alpha' (T - T_0)^2 \right\} \right]. \quad (9)$$

Eq.(9) can be used to obtain the values of interionic separation ( $r$ ) as a function of  $T$  provided  $\alpha'$  is known. For determining  $\alpha'$ , Kumar [14] used the following relationship at  $T = T_0$  based on the thermodynamic approximation considered by Dhoble and Verma [18]

$$(\alpha') = \alpha_0^2 M, \quad (10)$$

$$\text{where } M = [2 \delta_T - (dK_T/dP)] \quad (11)$$

and  $\delta_T$  is the Anderson-Gruneisen parameter defined as

$$\delta_T = -(1/\alpha K_T) (dK_T/dT)_P. \quad (12)$$

Using the values of  $\delta_T$ ,  $dK_T/dP$  and  $\alpha_0$  corresponding to temperature  $T_0$  as given in Table 1, we have calculated  $\alpha'$  from eq.(10) for eight alkali halides under study. These are also given in column (a) of Table 1.

Table 1. Values of input data for alkali halides under study [14,18]. Values of  $\alpha' = d\alpha/dT$  calculated from eq. (10) are given in column (a) and calculated from eq. (14) are given in column (b).

Crystals	$\alpha_0 (10^{-6} \text{K}^{-1})$	$dK_T/dP$	$\delta_T$	$M$	$\alpha' (10^{-8} \text{K}^{-2})$	
					a	b
NaF	96	5.28	5.84	6.40	5.8	5.3
NaCl	118	5.39	5.95	6.51	9.1	8.3
KCl	110	5.47	6.29	7.11	8.6	7.6
KBr	116	5.47	5.88	6.29	8.4	7.9
KI	123	5.55	5.83	6.11	9.2	8.8
RbCl	103	5.61	6.73	7.85	8.3	7.1
RbBr	108	5.59	6.64	7.69	8.9	7.7
RbI	123	5.60	6.53	7.46	11.0	9.8

It has been found by Anderson [1] that the product  $\alpha K_T$  does not change with temperature for solids at higher temperatures for  $T > \theta_D$ , i.e.  $\alpha K_T$  remains constant for the temperature range from  $T_0 = 300$  K upto the melting temperatures. Under this condition, one can obtain the relationship

$$\delta_T = dK_T/dP \quad (13)$$

which holds good for the solids under study and we can make use of this in eq.(10) to obtain the following simplified expression

$$(\alpha') = \alpha_0^2 \delta_T. \quad (14)$$

Values of  $\alpha'$  obtained from eq.(14) are given in column (b) of Table 1. Values of  $\alpha'$  based on eq.(10) are about 8 to 14 percent larger than the values estimated from eq.(14). It should be mentioned that eq.(10) is also an approximation, albeit less so than eq.(14).

### 3. Results and discussion

Values of input data used in calculations are given in Table 1. First, we demonstrate that the Kumar formulation is in error for  $\alpha(T)$ . Values of  $\alpha(T)$  calculated from eq. (1) are compared with the experimental values for NaCl and KCl in Table 2. They deviate much from the experimental data. On the other hand, the values of  $\alpha$  calculated from eq. (3) are closer to the experimental data. This justifies the correction made in the present study to the Kumar formulation of  $\alpha$ .

**Table 2.** Values of thermal expansivity  $\alpha$  ( $10^{-6}$  K $^{-1}$ ) for NaCl and KCl (a) calculated from eq. (1) and  $\alpha'$  from eq. (10), (b) calculated from eq. (3) and  $\alpha'$  from eq. (10), (c) calculated from eq. (3) and  $\alpha'$  from eq. (14) and experimental values [16,17].

#### NaCl

Temperature (K)	$\alpha$			Experimental
	a	b	C	
300	145	118	118	118
400	154	127	126	127
500	164	136	135	137
600	173	145	143	148
700	182	155	151	160

#### KCl

Temperature (K)	$\alpha$			Experimental
	a	b	C	
300	136	110	110	110
400	144	119	118	117
500	153	127	125	126
600	162	136	133	137
700	170	144	140	147

The experimental data on  $r(T)$  for the alkali halides under study, have been reported in the literature [2, 19, 20]. We have calculated the values of  $r(T)$  using the revised formulation [eq. (9)] and compared them with the experimental values (Table 3). The results can easily be obtained with the help of eqs. (2) and (9) using the input data given in Table 1. Here, we are giving the comparison of results only for some representative alkali halides. Similar results are obtained for other alkali halides also. We note

**Table 3.** Values of interionic separation  $r$  in Å at different temperatures  $T$  in K. Values given in column A are calculated using eq. (2) and  $\alpha'$  from column (a) of Table 1. Values given in column B and C are calculated using eq. (9) and  $\alpha'$  respectively from columns (a) and (b) of Table 1. Values given in column D are based on experimental data [16,17,20]

#### NaF

Temperature (K)	Interionic separation $r$ (Å)			
	A	B	C	D
300	2.318	2.318	2.318	2.318
400	2.327	2.326	2.326	2.326
500	2.336	2.334	2.334	2.334
600	2.346	2.342	2.342	2.342
700	2.357	2.351	2.351	2.351
800	2.368	2.361	2.361	2.361
900	2.379	2.371	2.370	2.371

#### KBr

Temperature (K)	Interionic separation $r$ (Å)			
	A	B	C	D
300	3.289	3.289	3.289	3.289
400	3.305	3.302	3.302	3.302
500	3.322	3.316	3.316	3.316
600	3.340	3.332	3.331	3.331
700	3.359	3.348	3.347	3.346
800	3.379	3.365	3.364	3.364
900	3.400	3.383	3.382	3.382

#### RbI

Temperature (K)	Interionic separation $r$ (Å)			
	A	B	C	D
300	3.668	3.668	3.668	3.668
400	3.688	3.684	3.684	3.683
500	3.709	3.701	3.701	3.699
600	3.732	3.720	3.719	3.716
700	3.756	3.740	3.738	3.734
800	3.782	3.761	3.759	3.753
900	3.809	3.784	3.782	3.774

from Table 3 for NaF, KBr and RbF that the values of  $r(T)$  calculated from eq. (9) are in closer agreement with the experimental values than those calculated from eq. (2). We have obtained two sets of results with the help of eq. (9) corresponding to two different values of  $\alpha'$  given in Table 1. The different values of  $\alpha'$  used as input in calculations, do not affect the final results appreciably. The difference in the values of  $\alpha'$  obtained from eqs. (10) and (14) is of the order of 10 % only. However, more important is the correction made in the Kumar formulation which replaces the factor  $(T^2 - T_0^2)$  appearing in the last term of eq. (2) by the factor  $(T - T_0)^2$  appearing in the last term of eq. (9). The effect of this modification increases with the increase in temperature. At the highest temperature  $T = 900$  K and  $T_0 = 300$  K considered in the present study, the value of the factor  $(T - T_0)^2$  is exactly fifty percent as compared to the value of  $(T^2 - T_0^2)$  appearing in the Kumar formulation. This correction of 50 percent is considerably higher than the difference of 10 percent in the values of  $\alpha'$  obtained from eqs. (10) and (14). In order to demonstrate this with more clarity, we have plotted the values of  $\Delta r = r(T) - r(T_0)$  where  $T_0 = 300$  K versus temperature in Figures 2–4 for NaCl, KI, and RbCl. Values of  $\Delta r$  represent the changes in interionic separations with the increase in temperature. The agreement for the values of  $\Delta r$  obtained from eq. (9) with the experimental data, as is evident from the figures, is much better than that for the values of  $\Delta r$  calculated from eq. (2).

#### 4. Conclusion

We have shown that the equation for thermal expansivity as taken by Kumar [14] is not consistent with the initial boundary condition viz.  $\alpha = \alpha_0$  at  $T = T_0$ . This yields the values of  $\alpha(T)$  and  $r(T)$ , which are not consistent with the experimental data. The Kumar formulation has subsequently been used by Pandey [21] for studying the thermal expansivity of NaCl at higher temperatures. Therefore, the study performed by Pandey is also subject to the same criticism. The formulation given by Kumar has been modified in the present study so as to make it consistent with the initial boundary condition. The modified formulation has been found to yield much improved agreement with the experimental data for  $\alpha(T)$  and  $r(T)$  of alkali halides at higher temperatures.

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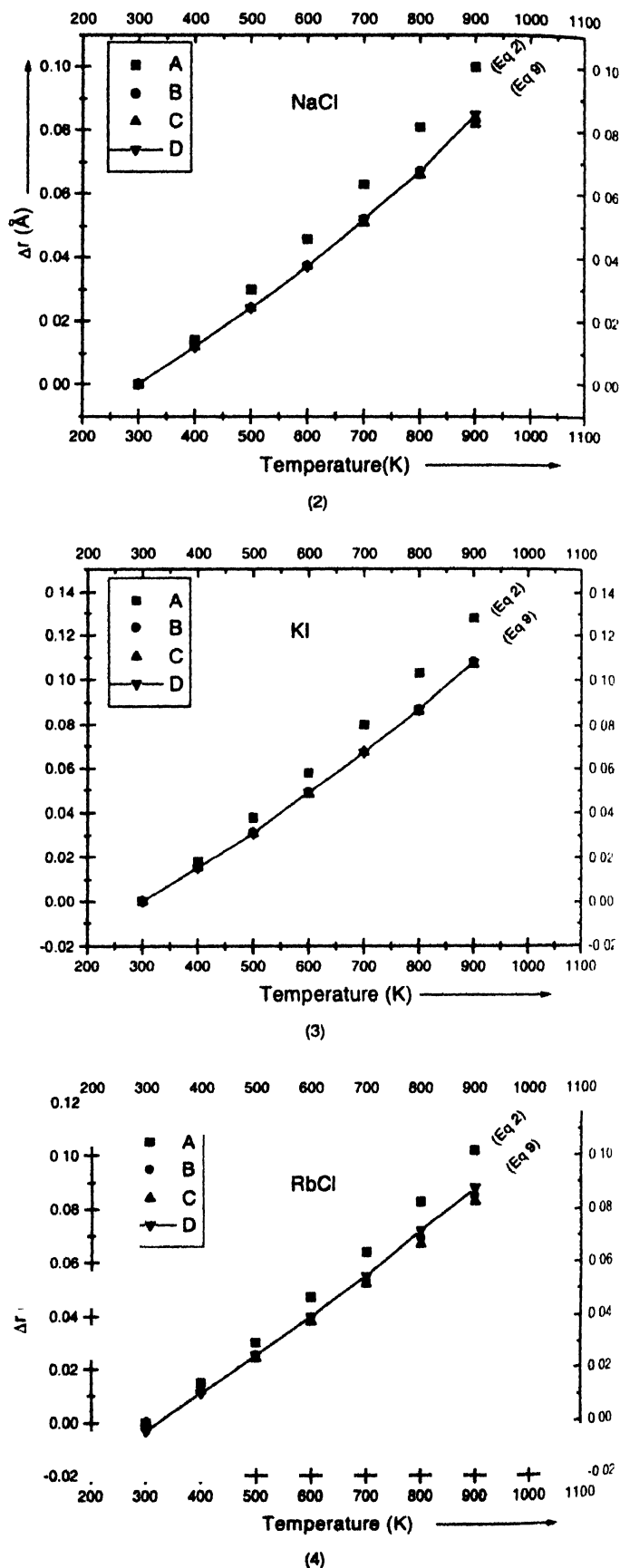


Figure 2-4. Plots of  $\Delta r = r(T) - r(T_0)$  in Å versus temperature  $T$  in K for NaF, NaCl, KCl, KBr, KI, RbCl, RbBr and RbI crystals. A, B, C, and D have the same meaning as described in Table 3. Experimental data [16,17,20] are shown by continuous curve.

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